Traces of stimulated bosonic exciton-scattering in semiconductor luminescence

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We observe signatures of stimulated bosonic scattering of excitons, a precursor of Bose-Einstein-Condensation (BEC), in the photoluminescence of semiconductor quantum wells. The optical decay of a spinless molecule of two excitons (biexciton) into an exciton and a photon with opposite angular momenta is subject to bosonic enhancement in the presence of other excitons. In a spin polarized gas of excitons the bosonic enhancement breaks the symmetry of two equivalent decay channels leading to circularly polarized luminescence of the biexciton with the sign opposite to the excitonic luminescence. Comparison of experiment and many body theory proves stimulated scattering of excitons, but excludes the presence of a fully condensed BEC-like state.

In the last few decades intensive theoretical and experimental work has been devoted to the understanding and observation of a macroscopic ground state of correlated electrons and holes in semiconductor structures. Analogous to Bose-Einstein-Condensation (BEC) of atoms, a dilute gas of bound electron-hole pairs - so called excitons - is predicted to condense into a common ground state [1, 2, 3]. Observation of condensation had been reported in CuO_2, where excitons with extraordinary long radiative lifetime exhibit signatures of BEC [4]. More recently, the observation of a macroscopically ordered state in a GaAs based heterostructures was interpreted in terms of exciton condensation [5]. However, all reports on possible exciton condensation are controversially discussed and alternative interpretations of the experimental data have been given [6, 7]. Clear criteria that are able to give unambiguous evidence for bosonic effects and ultimately BEC are therefore highly desirable. A precursor of excitonic BEC is stimulated scattering of excitons into other exciton states. The scattering rate is proportional to a bosonic enhancement factor $(1+n)$, where n is the number of excitons in the final state. In this letter we present experimental evidence for stimulated bosonic scattering in the exciton system of optically excited semiconductor quantum wells (QWs). The optical decay of a spinless biexciton (molecule of two excitons) into an exciton and a photon with opposite spin is subject to bosonic enhancement. The presence of spin polarized excitons causes the biexciton to decay preferentially into an exciton with the same spin. The resulting imbalance of circularly polarized photons in the final state leaves as signature a finite degree of circular polarization at the biexciton photoluminescence (PL) line. We report on clear experimental evidence for the described effect in semiconductor QWs. A full quantum mechanical many body model yields a criterion for bosonic effects which by comparison with our data proofs stimulated scattering but excludes the presence of a BEC-like state.

We investigate stimulated bosonic scattering in the photoluminescene of a high quality 10 nm thick ZnSe QW embedded in 500 nm $ZnS_{0.07}Se_{0.93}$ barriers grown by molecular beam epitaxy (MBE) on GaAs substrate [8]. The sample is kept in a finger cryostat and excited with frequency doubled fs pulses from an 80 MHz Ti:Sapphire laser through a microscope objective to obtain high exciton densities. The spectral width of the pulses is narrowed down to below 4 meV by means of a pulse shaper to allow for resonant excitation of bound electrons and holes close to the exciton resonance which avoids the creation of hot carriers with excess energy. The polarization of the exciting light is carefully controlled by a Soleil-Babinet retarder. The semiconductor luminescence is measured in reflection geometry by a synchroscan streakcamera providing a spectral and temporal resolution of 2 meV and 6 ps, respectively. By passing the PL through an electrically tunable liquid-crystal retarder, the left and right circularly polarized components are separately measured without artifacts from possible beam displacement known from traditional optical elements like a $\lambda/4$-wave-plate.

We optically excite excitons with angular momentum $J_z = 1$ by pumping the sample with circularly polarized laser pulses of about 2 ps duration. Excitons with $J_z = -1$ are also created due to imperfect selection rules and spin relaxation. Subsequently biexcitons are formed by binding of excitons with opposite angular momentum. Excitons with parallel angular momenta cannot form a bound state. The spin related criteria for binding are analogous to hydrogen where only atoms with antiparallel electron spin form molecules. Figure 1(b) depicts a PL spectrum 20 ps after excitation at a sample temperature of 10 K. The high energy luminescence peak results from the optical recombination of excitons. Because of the small photon momentum only excitons with momentum $K \approx 0$ contribute to the emission. The low energy luminescence peak results from the decay of a biexciton into a photon and a free exciton. The energetic position of the peak is at $E_x - \delta_{\mathrm{bi}}$, where E_x is the exciton energy and δ_{bi} is the biexciton binding energy. Because the biexciton consists of two excitons with opposite angular momenta, one decay channel results in an emitted σ^+ polarized photon and a remaining $J_z = -1$ exciton, whereas the other channel yields the opposite angular momenta (σ^- and $J_z = 1$). Within a four level scheme, the aver-

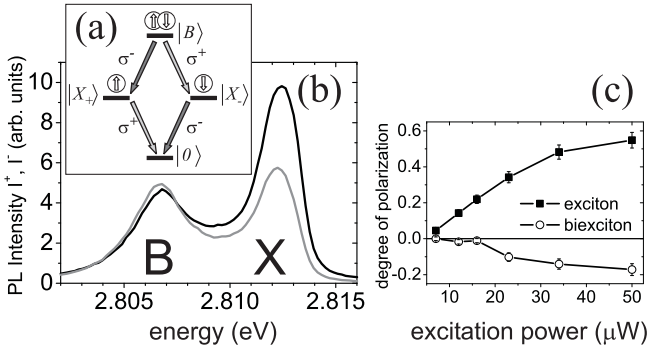

FIG. 1: a) optical decay scheme, b) polarization resolved PL spectrum at T =10 K, 20 ps after laser excitation. Black line: σ^+ polarization. Gray line: σ^- polarization. c) density dependence of polarization 15 ps after excitation, exciton (full squares) and biexciton (open circles).

age optical emission of biexcitons should be completely unpolarized [Fig. 1(a)].

In contrast, we find for high excitation densities *circular polarized emission* at the biexciton line, whose sign is *opposite* to that of the excitons. Figure 1(b) shows the circular polarized PL spectrum 20 ps after quasi resonant excitation of the exciton resonance with 50 μW creating an estimated exciton density of about 8×10^{11} cm^{-2}. The time delay guarantees that the initial coherence of laser pulse and excitons has completely vanished. The spectrum clearly shows the polarization effect. The magnitude of biexciton polarization increases with increasing exciton density from zero to about 17 % [Fig. 1(c)]. The simultaneous increase of polarization at the exciton can be explained by the increasing fraction of excitons with opposite spin that are bound into biexcitons and therefore do not contribute to excitonic emission with opposite circular polarization. For low densities, the degree of exciton polarization is much lower than expected from the selection rules. We explain this by a short electron spin relaxation time τ_s which decreases from about 100 ps to 20 ps at lowest densities [9]. Independently, we observed the same biexciton polarization effect also in 5 nm ZnSe/ZnMgSSe multiple QWs and in a 9.9 nm GaAs/AlAs single QW.

In the following we exclude a number of artifacts that might have caused the polarized emission at the biexciton line. (i) Creating excitons with opposite circular polarized laser pulses changes both, the sign of exciton and biexciton photoluminescence. This exclude that the biexciton polarization is caused by some polarizing element in the optical path of the luminescence or by some asymmetry which could have favored negative polarization. Similarly, the application of an in-plane magnetic field leads to spin-oscillations which modulate both the exciton and biexciton polarization with the same frequency [10]. (ii) The optical dielectric function of a QW is after excitation with circular polarized light no longer the same for σ^+ and σ^- polarized light. Since the rate of spontaneous emission depends on refractive index and reabsorption, we calculated emission at the biexcitonic line taking into account the polarization dependent dielectric function and the dielectric properties of the sample structure [11]. We found a low degree of polarization induced by the spin dependent sample properties, that, however, exhibited the same sign as the exciton polarization. I.e., the surprising polarization effect of the biexciton may be even larger than it appears from the bare luminescence data. (iii) A large energetic spin splitting of the exciton levels induced by exchange interaction would lead to energetically distinct fully polarized biexciton lines with equal intensity, but no average polarization. A finite splitting could therefore explain polarized emission in the low energy tail of the biexciton line. This artifact is excluded, because, first, there is no visible splitting of the $\sigma^\pm$ exciton lines, and, second, integration over the full biexciton line still exhibits polarized emission.

We will first give a preliminary explanation of polarized emission at the biexciton line based on the Dicke theory of spontaneous emission, which originally was developed to treat cooperative optical decay of several multi-level atoms in a small volume [12, 13, 14]. Consider a chain of N adjacent sites which can be occupied by an exciton with either spin 1, spin -1, or a biexciton [15]. The chain may be viewed as a quantum wire with the length of N exciton units and periodic boundary conditions. In this picture the decay of an exciton at a certain site corresponds to the transition from an excited atomic level $|X_{j,\pm}\rangle$ to the ground state $|0_i\rangle$. The PL intensity of the full exciton chain at the exciton line is given by $I_\pm = \langle R_\pm^\dagger R_\pm \rangle$, where $R_\pm = \sum_{i=1}^N |0_i\rangle\langle X_{i,\pm}|$ is the macroscopic dipole operator of all N excitons and i labels the exciton sites. Photon emission at the biexciton line is linked to the annihilation of a biexciton, $X_{j,+}X_{j,-}$, and the creation of an exciton, $X_{j,+}^\dagger$, and a photon with opposite angular momentum. Within the Dicke formalism one needs to calculate $I_{\mathrm{b},\pm} = \langle R_{\mathrm{b},\pm}^\dagger R_{\mathrm{b},\pm} \rangle$, where the macroscopic dipole operator $R_{\mathrm{b},\pm} = \sum_{j=1} X_{j,\mp}^\dagger X_{j,+} X_{j,-}$ is now expressed in second quantization with the operator relations $X_{i,\pm}X_{j,\pm} = X_{j,\pm}X_{i,\pm}$ and $X_{i,\pm}^2 = 0$ (hard core bosons). Exciton and biexciton operators can be defined in momentum space $x_{k,\pm} = N^{-1/2}\sum_{j=1}^N X_{j,\pm}\exp(2\pi ikj/N)$, $b_k = N^{-1/2}\sum_{j=1}^N X_{j,+}X_{j,-}\exp(2\pi ikj/N)$ with $k = 0, ..., \pm(N-1)/2$, which is closer to the usual notation in semiconductor theory. In this representation we find for biexciton luminescence $I_{\mathrm{b},\pm} = \sum_{k,k'}\langle b_k^\dagger x_{k,\mp} x_{k',\mp}^\dagger b_{k'}\rangle$, implying momentum conservation as expected. For calculating PL of a sample with incoherent excitons and biexcitons we can drop off-diagonal terms with $k \neq k'$. We proceed calculating the k-dependent terms $I_{k,\pm} = \langle b_k^\dagger x_{k,\mp} x_{k,\mp}^\dagger b_k\rangle$ by applying the exact Bose-commutation

relations $x_{k,\mp}x^\dagger_{k,\mp} - x^\dagger_{k,\mp}x_{k,\mp} = 1 - 2n_\mp/N$, where the number operator $n_\mp = \sum_k x^\dagger_{k,\mp}x_{k,\mp}$ counts all excitons with the same spin (including excitons bound in biexcitons). After approximating the four operator expectation values by factorized products, the biexciton PL intensity obtains the final form

$$\begin{aligned} I_{k,\pm} &= \langle b^\dagger_k(1 + x^\dagger_{k,\mp}x_{k,\mp} - 2n_\mp/N)b_k\rangle \\ &\approx \langle b^\dagger_k b_k\rangle \left(1 + \langle x^\dagger_{k,\mp}x_{k,\mp}\rangle - 2\frac{\langle n_\mp\rangle}{N}\right). \end{aligned} \quad (1)$$

It follows that biexciton emission $I_{k,\pm}$ depends not only on the occupation of biexcitons $\langle b^\dagger_k b_k\rangle$ but also on a enhancement factor $\left(1 + \langle x^\dagger_{k,\mp}x_{k,\mp}\rangle - 2\langle n_\mp\rangle/N\right)$. We interpret this factor as stimulated bosonic scattering of final state excitons with momentum k into excitons that were already present in the state k. This immediately explains the negative circular polarized biexciton PL in the presence of spin polarized excitons with positive angular momenta $\langle x^\dagger_{k,+}x_{k,+}\rangle > \langle x^\dagger_{k,-}x_{k,-}\rangle$. Similarly, positive circular polarization is observed in the presence of excitons with negative angular momenta. Only for highest exciton densities [$\langle n_\mp\rangle/N \approx 50\%$] the third term of the enhancement factor may dominate and lead in special cases to polarized biexciton emission with the same sign as the excitons. Our observations exhibit a clear deviation of the usual proportionality between occupation number and PL intensity in semiconductors (without a laser-like optical feedback).

The derivation above already gives a good impression of the origin of the polarization effect. However, the calculation does not regard exciton energy dispersion, and makes no prediction about the actual exciton-biexciton distribution which at high densities is not simply described by a Bose-Einstein distribution. Excitons are no ideal bosons and the Pauli exclusion principle applies to their fermionic constituents, electrons and holes. Inclusion of such features is unfortunately beyond the applicability of full microscopic theories of semiconductor luminescence that neglect spin and correlations related to biexcitons [16, 17, 18, 19]. We therefore introduce a simplified model Hamiltonian for a 1D exciton biexciton system

$$H = \sum_{k,\sigma=\pm} E_k x^\dagger_{k,\sigma}x_{k,\sigma} - \sum_j \delta_\mathrm{b} X^\dagger_{j,+}X_{j,+}\, X^\dagger_{j,-}X_{j,-}, \quad (2)$$

that quantitatively includes the exciton dispersion E_k. Biexciton formation is included by a short range (on-site) potential well with depth $-\delta_\mathrm{b}$, which in principle allows for a biexciton state that extends in contrast to the Dicke model over more than just one site. The distance between two adjacent sites is assumed to be four exciton Bohr radii $4a_0$, which correspond to kinetic exciton momenta of $p_k = \pi\hbar k/2a_0N$ [20]. We obtain with the experimental values for exciton radius $a_0 = 5$ nm and

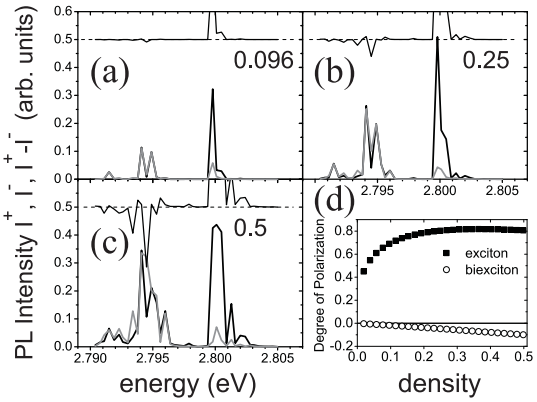

FIG. 2: a)-c) Calculated polarized PL spectra I^+, I^-, and $I^+ - I^-$ (offset by 0.5 for better visibility) at T = 15 K for increasing densities of 0.096, 0.25, and 0.5 excitons per site. d) density dependence of the excitonic and biexcitonic degree of polarization.

the exciton mass $m_X = 0.344m_0$ the exciton dispersion relation $E_k = E_\mathrm{X} + p_k^2/2m_X$ with a maximum kinetic energy of about $E_\mathrm{max} = 11$ meV and $E_\mathrm{X} = 2.8$ eV. In order to calculate the luminescence spectrum of the system at a given temperature, we calculate the multi particle density matrix

$$\rho \propto \exp\left(-\frac{1}{k_\mathrm{B}T}\left(H - \mu_+n_+ - \mu_-n_-\right)\right) \quad (3)$$

where μ_+ and μ_- are the chemical potentials which govern the average number of spin up $\langle n_+\rangle$ and spin down $\langle n_-\rangle$ excitons. The intensity of $\sigma^\pm$ polarized PL emitted by decay of a multi-particle energy eigenstate $|\psi_i\rangle$ into a state $|\psi_f\rangle$ is given by $I^\pm_{i,f} = |\langle\psi_f|D_\pm|\psi_i\rangle|^2$, where $D_\pm = d\sum X_{j,\pm}$ is the overall dipole operator (in rotating wave approximation). Consequently, the full polarized luminescence spectrum that belongs to the mixed state ρ is given by

$$I_\pm(\epsilon) = \sum_{i,f}\langle\psi_i|\rho|\psi_i\rangle\,|\langle\psi_f|D_\pm|\psi_i\rangle|^2\,\lambda\left(\epsilon - (\epsilon_i - \epsilon_f)\right), \quad (4)$$

where λ has the homogenous linewidth of an optical emission event and ϵ_i is the energy of the multi-exciton states. Figure 2 shows the calculated PL spectra for σ^+ and σ^- polarization for the model with $N = 5$ sites ($2^{2\cdot5} \times 2^{2\cdot5}$ density matrix) at a temperature of $T = 15$ K and with a fixed spin polarization $(\langle n^+\rangle - \langle n^-\rangle)/(\langle n^+\rangle + \langle n^-\rangle) = 0.25$. At low densities $\langle x^\dagger_{k,\mp}x_{k,\mp}\rangle \ll 1$ there is almost no biexciton polarization effect as expected [compare eq. (1)]. At elevated densities, the polarization effect increases significantly to up to 10 % at a density of 0.5 excitons per site (2.5 excitons distribute over all 5 sites), which corresponds to about 1.25×10^{12} cm^{-2}. The calculated magnitude of the biexciton polarization effect in the different density regimes compares qualitatively well

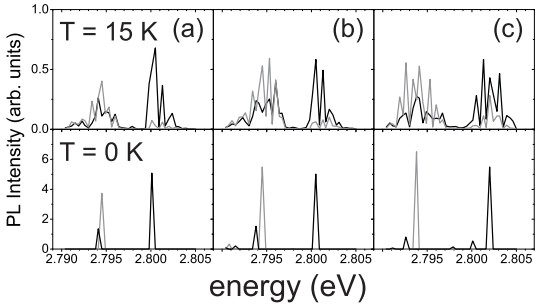

FIG. 3: Calculated PL spectra at T = 15 and T = 0 K. a) Number of excitons $(n_+, n_-) = (2,1)$ b) (3,2) c) (4,2).

with experiment. Also the relative height of exciton and biexciton peak compares well with our measurement. We obtain improved agreement with data if we assume an exciton temperature of $T = 30$ K in the calculations, which can be understood by the increase of carrier temperature during the binding process of biexcitons.

Next we discuss criteria to observe BEC-like condensation in the exciton biexciton system. First we show that the calculated ground state of our model Hamilton can be well approximated by an analytical expression which has the from of a phase average BCS-like state (BCS state becomes a BEC state in the low density limit)

$$|\psi(\phi_1,\phi_2)\rangle \propto \prod_{i=1}^{N}\left(1 + c_1 e^{i\phi_1} X^\dagger_{i,+} + c_2 e^{i\phi_2} X^\dagger_{i,+} X^\dagger_{i,-}\right)|0\rangle, \tag{5}$$

which contains excitons and biexcitons as condensing entities with two macroscopic phases ϕ_1 and ϕ_2. Since the Hamilton H commutes with the particle operators $n_\pm$, the ground state is required to posses sharp particle numbers which we obtain by phase-averaging $|\psi(\phi_1,\phi_2)\rangle$

$$|\Phi(n,m)\rangle \propto \int_{\phi_1,\phi_2=0}^{2\pi} |\psi(\phi_1,\phi_2)\rangle e^{-i(n-m)\phi_1 - im\phi_2} d\phi_1\, d\phi_2, \tag{6}$$

where n and m are the number of excitons with spin 1 and spin -1, respectively. The overlap $\alpha = |\langle\Phi(m,n)|\chi(m,n)\rangle|^2$ of the BCS-like state with the numerically gained ground states $|\chi(m,n)\rangle$ exhibits good agreement (α ranging from 0.6 and 1.0). The calculated emission spectra for $|\chi(m,n)\rangle$ with $n > m$ reveal at $T = 0$ sharp peaks at the exciton and biexciton energy [fig. 3, bottom row]. The biexciton peak shows a high degree of polarization which increases with density. The presence of strongly polarized biexciton emission is a clear signature for a highly correlated multi exciton state. The exciton peak is 100 % polarized, because all minority excitons with opposite spin form a biexciton at zero temperature. For comparison, a system with the same average exciton densities, but $T = 15$ K exhibits broad spectral features and a much lower degree of polarization at the biexciton and exciton resonance [fig. 3, top row]. Consequently, we suggest as a criterion for a condensed system of partially polarized exciton the observation of sharp PL lines with a high degree of polarization at the exciton *and* biexciton emission PL line. This criterion is experimentally less demanding than the suggested measurement of the photon statistics of emitted light [18, 19]. Applying the criterion to our data, we conclude that we observe stimulated bosonic scattering of excitons, but do not observe a fully condensed multi-exciton state.

In conclusion we found unambiguous traces of stimulated bosonic scattering of excitons in the photoluminescence of a photo-generated exciton biexciton system. The spectral signature at the biexciton line is explained in terms of cooperatively radiating excitons and biexcitons within Dicke theory and numerically treated within a many body theory which yields all major features of our experimental observations.

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